



## Soybean and coconut oil based unsaturated polyester resins: Thermomechanical characterization



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### ABSTRACT

This paper reports the development of new unsaturated polyesters resins (UPRs) based on soybean oil and coconut oil. Unsaturated polyesters (UPs) were firstly synthesized by polycondensation from renewable monomers and were further crosslinked using styrene. The chemical structure of the new UPs was confirmed by attenuated total reflectance Fourier Transform Infrared (ATR-FTIR) and by proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR) spectroscopies. The thermal and mechanical properties of the UPs and UPRs were studied by thermogravimetric analysis (TGA) and by dynamic mechanical thermal analysis (DMTA) to evaluate the impact of the incorporation of renewable monomers in the properties of the materials. TGA analysis revealed that bio-based UPs are thermally stable until temperatures of 250 °C. The  $T_g$  values obtained for these new UPs varied between –11 °C and 2 °C, being the UP composed by bio-based soybean oil and propylene glycol the resin with the highest  $T_g$ . As expected, after crosslinking UPRs showed to be thermally more stable than the UPs. The DMTA analysis revealed that the  $E'$  and the  $T_g$  could be easily tailored by varying the monomers in the formulation.

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### 1. Introduction

Currently, unsaturated polyester resins (UPRs) are one of the most important classes of thermoset polymers in the industry. Due to the excellent balance between their mechanical, electrical and chemical properties and their low cost, these polymers are widely used as coatings and composite materials in construction and in the marine and automotive industries (Mustapha et al., 2014; Sanchez et al., 2000). In the industry of UPRs, maleic anhydride (MA), phthalic anhydride (PhA) and propylene glycol (PG) are the most regularly employed raw materials (Matynia et al., 2006; Rogers and Long, 2003). However, in the last years, due to environmental and sustainability issues, the replacement of fossil-based monomers by their renewable counterparts have been the focus of several studies (Dai et al., 2015; Gonçalves et al., 2014; Jasinska and Koning, 2010a,b; Sadler et al., 2014). Other promising strategy to increase the 'green content' of the polymers concerns the incorporation of vegetable oils, which are readily available and inexpensive

materials (Gobin et al., 2015; Liu et al., 2014; Lligadas et al., 2013; Miyagawa et al., 2006; Mustapha et al., 2014; Qin et al., 2011).

A variety of oils like palm, linseed and casor oil have already been used for the synthesis of bio-based UPs and UPRs (Dutta et al., 2004; Lai et al., 2013; Liu et al., 2014; Mahmoud et al., 2011; Miyagawa et al., 2006). Soybean oil (SO), particularly, is a vegetable oil with interest in the polymers industry because of its abundant availability, reactive functionalities and competitive cost (Biswas et al., 2008; Miao et al., 2014). This renewable material is constituted by triacylglycerols with a mixture of fatty acids, being 51% of linoleic acid and has about 4.5 double bonds per molecule.

SO has been used in the manufacturing of plastics, adhesives, for coating applications and also to prepare oil-based UPs (Biswas et al., 2008; Miao et al., 2014; Qin et al., 2011). Miyagawa et al. (2007) developed UPRs making use of a mixture of a fossil based UP diluted in styrene with epoxidized methyl soyate (EMS), which is a mixture of epoxidized fatty methyl esters. The authors evaluated the effect of increasing amount of EMS on the thermomechanical properties of the resulting materials. The results showed a decrease in the storage modulus and in the heat deflection temperature as the amount of EMS increased in the formulation. In turn, the Izod impact strength value did not change for higher amounts of EMS. SO was also used by Qin et al. (2011) to obtain bio-based UPRs.

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A monoglyceride mixture was firstly obtained by transesterification between glycerol and soybean oil and, in the second step, this mixture was reacted with PG, MA and PhA. The mechanical properties of the UPs were later evaluated in the second contribution reported by Li et al. (2011). According to the authors, using styrene as the diluent and with a content of SO monoglyceride between 15 and 20%, resins with good impact strength, tensile strength and flexibility were obtained. Also, cured resins present a lower curing shrinkage (4%) compared with commercial UPR.

Besides SO, coconut oil (CO) is also an abundant natural source with a relatively low cost, being largely used in cosmetic and pharmaceutical industries and much less explored in the UPRs synthesis (Kumar and Krishna, 2015). Since CO is mainly composed by saturated fatty acids (>91%), it is not explored in the synthesis of crosslinked resins (Dayrit, 2015). However, the presence of non-crosslinked carbon chains would be favorable to prepare materials with relatively high impact strength. Fig. 1 presents the structures of the vegetable oils used in this work.

In this work different UPs with high “green” content based on SO and CO were prepared. These structures were further crosslinked in order to access the effect of unsaturation level on the thermo-mechanical properties of the UPRs.

## 2. Experimental

### 2.1. Materials

Soybean oil (SO), coconut oil (CO), ethylene glycol (EG, 99,8%), 1,2-propanediol (PG, 99%), styrene (Sty, >99%), tetrahydrofuran (THF, >95%), *p*-xylene (99%), methyl ethyl ketone peroxide (MEKP) and 2-ethoxy ethanol were purchased from Sigma–Aldrich. Maleic anhydride (MA, >99%), phthalic anhydride (PhA, 99%) and 1,3-propanediol (PDO, >98%) were purchased from TCI Europe. Succinic acid (SuA, 99%) and potassium hydroxide solution (1N, in ethanol) were purchased from Acros Organics. Cobalt octoate (CoO, 1%w/v in xylene) was purchased from AGAMI, phenolphthalein was obtained from Riedel-de-Häen. Hydroquinone (HQ) was purchased from Analar. Deuterated THF (THF-*d*<sub>8</sub>, 99,5%, 0.01% TMS) was purchased from Eurisotop. All the reactants were used as received, unless otherwise stated.

### 2.2. Synthesis of bio-based unsaturated polyesters

The SO and CO-based unsaturated polyesters (SO.UP and CO.UP) were prepared by bulk polycondensation. Briefly, the monomers and a radical inhibitor (HQ, 0.01 wt% relative to the monomers in the feed) were charged into a four-necked glass reactor, equipped with a mechanical stirrer, a nitrogen inlet and a condenser connected to a round-bottom flask. The polycondensation reactions at a maximum temperature of 205 °C. Water was distilled during reaction. The end of reaction was set when the acid value (AV) reached a value of ca. 30 mg KOH/g (according to ASTM 109-01). Table 1 presents the molar amounts of the monomers in the feed, the AV values and the final viscosity values of the different UPs.

### 2.3. Preparation of the UPRs

The SO.UPs and CO.UPs were dissolved in 35 wt% St. The initiator MEKP (2 wt%) and accelerator CoO (0,2 wt%) were added under continuous stirring until a homogeneous mixture was obtained (Martín, 1999). The formulations were cured in a Teflon mold (16 × 7 × 0.5 mm) at room temperature for 12 h and post-cured at 80 °C for 3 h, for the obtainment of SO.UPRs and CO.UPRs (Atta et al., 2007; Lai et al., 2013).

### 2.4. Characterization

#### 2.4.1. Chemical characterization

The chemical structure of the UPs was confirmed by Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) and Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR) spectroscopies. ATR-FTIR analysis was carried out with a Jasco FT-IR-4200 spectrometer, equipped with a Golden Gate Single Reflection Diamond ATR. Data collection was performed with 4 cm<sup>-1</sup> spectral resolution and 64 accumulations.

<sup>1</sup>H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer using a 5 mm TIX triple resonance detection probe, in THF-*d*<sub>8</sub>, at room temperature. Tetramethylsilane (TMS) was used as the internal reference.

#### 2.4.2. Thermal and mechanical properties

The thermal stability of samples was evaluated by thermogravimetric analysis (TGA), using a TA Instruments Q500 thermogravimetric analyzer (thermobalance sensitivity: 0.1 μg). The equipment was calibrated within a temperature interval ranging from 25 °C to 1000 °C, at a heating rate of 10 °C min<sup>-1</sup>, running tin and lead as melting standards. The samples were analyzed using open alumina crucibles, in the temperature range 25–600 °C and at a heating rate of 10 °C min<sup>-1</sup>, under dry nitrogen purge flow of 100 mL min<sup>-1</sup>.

The viscoelastic properties of the UPs and UPRs were measured by dynamic mechanical thermal analysis (DMTA) with a Tritec 2000 DMA. SO.UPs and CO.UPs were analyzed in the single cantilever bending geometry using stainless steel material pockets. The properties of SO.UPRs and CO.UPRs were analyzed in the dual cantilever bending geometry. All DMTA measurements were carried out in a –150 °C to 200 °C temperature range, at frequencies of 1 and 10 Hz, using a heating rate of 5 °C min<sup>-1</sup>. The glass transition temperature (*T*<sub>g</sub>) was determined as the peak maximum in tan δ curve, at the frequency of 1 Hz.

#### 2.4.3. Viscosity

The kinematic viscosity of synthesized UPs was determined by Gardner–Holdt Bubble Viscometer. The sample is placed into a standard viscosity tube and is thermostated at 25 °C. The viscosity of the sample is determined by comparison to the standard bubble viscometer tubes (or Gardner–Holdt tubes) with standard viscosity marked alphabetically, in which an air bubble rises with the same speed as it does in the tube of the sample being tested. The standard tube with the same viscosity as the sample has a letter that can be converted to the kinematic viscosity, in Stokes (St) (Joseph, 2012). The viscosity of all polyesters was determined in a 50% solution by weight of the UP in 2-ethoxyethanol (adapted from Papparatto et al., 1978).

#### 2.4.4. Gel content

The gel content (according to ASTM D2765) was determined by Soxhlet extraction using THF as solvent. The samples were weighed and placed in the Soxhlet's extractor for 8 h. After that, the samples were dried until constant weight, and weighed. Gel content was calculated according to Eq. (1):

$$\text{Gel Content} = \frac{w_f}{w_0} \times 100 \quad (1)$$

where *w*<sub>0</sub> and *w*<sub>f</sub> represent, respectively, the weight before and after extraction.

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